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14. ABSTRACT In this project we introduced a new approach to obtain nanostructured organic-inorganic ceramic materials using the sol-gel method combined with high-pressure technique to produce ceramics with multifunctional properties. We investigated hybrid nanostructured materials, exploring alumina, zirconia and silica systems using carbon nanotubes (CNTs) as nanofibers reinforcements. The main challenge in CNTs-reinforced ceramic nanocomposites is the uniform dispersion of CNTs into the ceramic matrix and to obtaining a good interface between the CNTs and the matrix. This step is fundamental and we were able to achieve that. It was produced powders of nanocomposite materials of CNT/alumina and CNT/zirconia. This materials and its applications are the subject of two PhD Thesis, that should be finished by the middle of 2012. several works were already published on this matter and some were presented in International Meetings.					
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## **Context and Objectives**

The subject of this project supported by the AFOSR is to obtain nanostructured organic-inorganic ceramic materials using the sol-gel method combined with high-pressure technique to produce ceramics nanocomposites with multifunctional properties exploring mainly alumina and zirconia and using carbon nanotubes (CNTs) as nanofibers reinforcements.

In conventional hybrid materials, where the reinforcing elements are typically in the micrometer scale, as glass fibres, carbon fibres and Kevlar® fibres, the resultant composites are multifunctional and have remarkable properties, such as being stiff but light weight. In the case of nanocomposites, it is possible to make materials with improved mechanical or electrical properties. Also nanoreinforcements produce small local stress concentrations, facilitating composite processing and increasing the toughness of the material.

However, to obtain these nanocomposites of CNTS/ceramic matrix, there is a challenge: a uniform distribution and a good dispersion of the CNTs reinforcements into the matrix are prerequisites for the high-performance of a composite material, as well as a very good interface between the CNTs and the matrix must be achieved. Hence, our primary goal was to obtain a good dispersion of CNTS in aqueous solutions that could be used in sol-gel synthesis to produced nanocomposites powders of both ceramics: alumina and zirconia. In order to do that, several surfactants were investigated.

Our final goal is to produce nanocomposites from the powders obtained by sol-gel process by compaction at high-pressure and high-temperature, aiming to produce nanocomposites with novel properties, having higher thermal and electrical conductivities, resulting in multifunctional materials with alterations in their electrical and thermal properties upon addition of the CNTs.

## **People Involved**

Our group, in this project, is composed by the PI (Marcia R. Gallas), Co-PI (Tania M. H. Costa), three PhD students doing thesis work: Patricia R. Silva, Voltaire de O. Almeida, and recently (march 2011) Pamela M. dos Santos; two Master students, that finished their dissertations: Marina T. Laranjo and Pamela Mantey dos Santos; two undergraduate students: Wagner R. Fagundes and Giovanni R. Rodrigues (with a scholarship from this project).

During the current Project, the Master dissertation of M. T. Laranjo about hybrid materials of silica and gold nanoparticles was concluded in December 2009 and also, P. M. do Santos finished her Master dissertation, about the behavior of carbon nanotubes processed at high-pressure, in December 2010. The Master Degree is a mandatory requirement in Brazil, before the PhD.

Thanks to the AFOSR Contractor's Meeting of High Temperature Aerospace Materials, in 2010, we also started collaboration with Dr. Arvind Agarwal from the Mechanical and Materials Eng. Department of Florida International University (FIU), Miami.

## **Research Efforts**

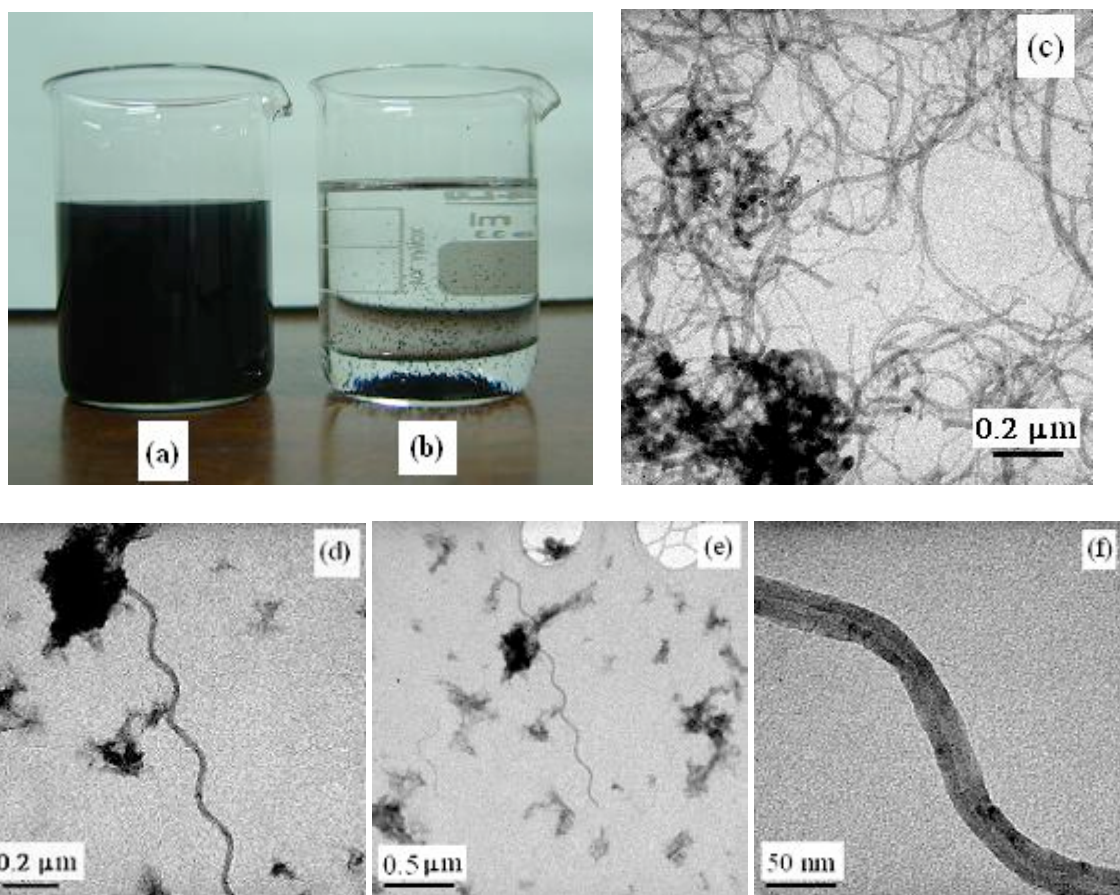
During the last decade, ceramic matrices composites reinforced by CNTs have been extensively studied, aiming to improve the intrinsic brittleness of these materials. Among ceramics, alumina and zirconia are of great interest because of their numerous applications in several fields, for example as refractory materials. However, to produce these composites, the CNTs must be processed in such a way to ensure that a homogeneous dispersion is obtained within the matrix, whilst developing an appropriate degree of interfacial bonding.

A fair amount of research has been conducted on dispersion of CNTs based on both physical and chemical approaches. Chemical functionalization was proposed as a promising method to improve the dispersion of CNTs in organic solvents as well as in aqueous media. However, this method showed that

covalent surface functionalization can affect inherent electrical, mechanical, and optical properties of CNTs. Hence, several studies were concentrated on noncovalent modifications, and the use of surfactants to stabilize CNTs suspension becomes an efficient approach.

The surfactant choice basically depends on the kind of solvent that is used to disperse the CNTs, the type of matrix (polymeric or ceramic) the CNTs will be incorporated, and what properties you want to improve. The development of a surfactant that can enhance the CNTs solubility in generic nonpolar organic solvent is of great interest, especially for the composite fabrication using the sol-gel processing method. Particularly, in the case of alumina ( $\text{Al}_2\text{O}_3$ ), and zirconia ( $\text{ZrO}_2$ ), matrices produced by the sol-gel method, the right choice of surfactant is critical.

Recently a silica-based hybrid xerogel was synthesized that contains the double-charged group diazoniabicyclo[2.2.2]octane chloride, bonded to the silica moiety in a bridged way by some collaborators in the Chemistry Department of our University. An important characteristic of this material is that it has a specific affinity for aluminium, possibly forming a Si-O-Al bond, and it was already used as protective coating for aluminium surfaces. Based on this specific affinity, we propose a preparation and application of a new ionic surfactant as a dispersant for CNTs in ceramic matrices. It contains a stearate-based 18-carbon alkyl chain as anion (octadecanoic acid), which makes hydrophobic interaction with side walls of CNTs, and a silsesquioxane containing a bridged, positively charged 1,4-diazoniabicyclo[2.2.2]octane group, which presents high affinity for aluminum. We called it dabcosil stearate (Db-St). Multi-walled carbon nanotubes (MWCNTs) were used to prepare our MWCNT/alumina and MWCNT/zirconia composites by the sol-gel method using the Db-St as the dispersant agent for the MWCNTs. Some of our results for the dispersion of MWCNTs can be seen in the images below.

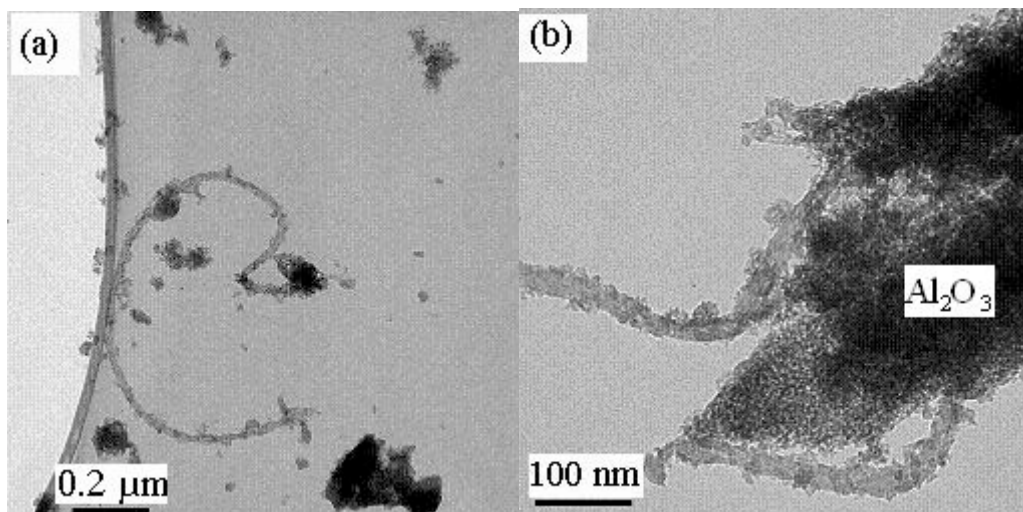


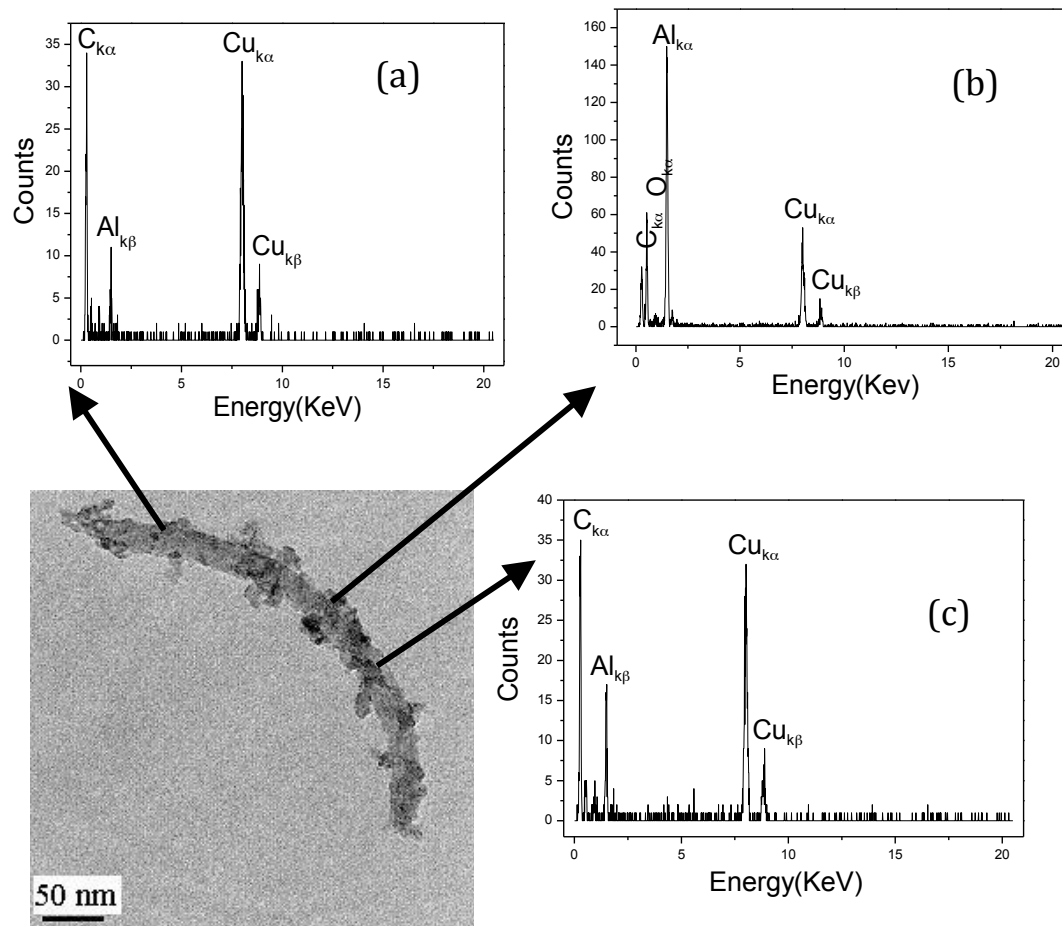
In Figure (a) we can observe a stable black suspension of the MWCNTs in the surfactant solution of Db-St, whereas in Figure (b) we clearly see that the MWCNTs are precipitating to the bottom, using the same concentration of MWCNTs, but only in butyl alcohol. In Figure (c), the TEM image shows a tangle of MWCNTs and the diameter of the pristine MWCNTs was estimated to be between 10 and 40 nm. In Figure (d), at the same magnification, we see an individually dispersed MWCNT. It is important to point out that these two TEM images are representative of all regions we investigated indicating that effectively it was possible to isolate one MWCNT using this surfactant. Figure (e) shows a TEM image with a lower magnification of the same region showed in Figure (e), and it is possible to observe that there is another MWCNT, also isolated in that region. Figure 1f shows a higher magnification, where we can estimate the diameter of the MWCNT as about 30 nm, in the same diameter range of the pristine MWCNTs. Also we can observe that the MWCNT is not damaged,

maintaining its integrity. Several TEM images were taken in different regions, and with different magnifications, being similar to the ones that are showed here.

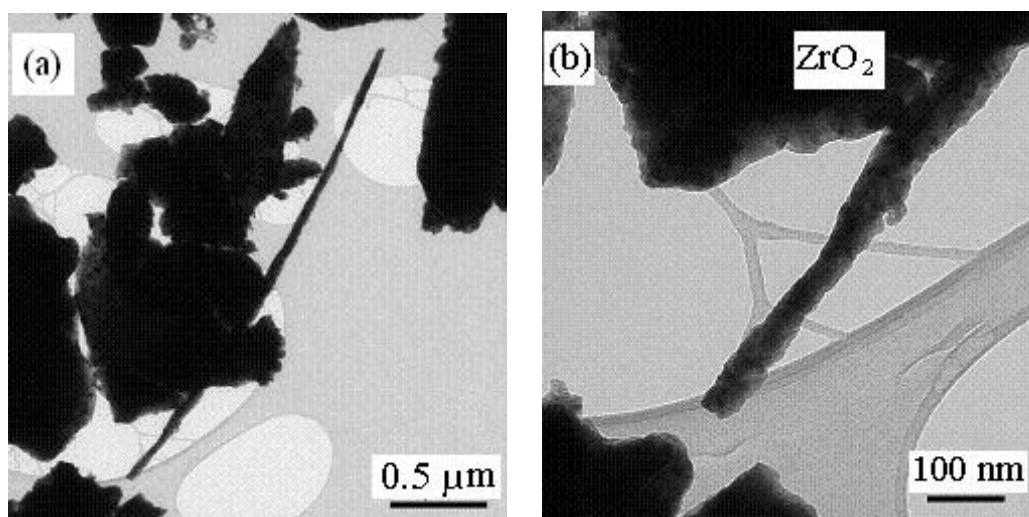
### **MWCNTs/Alumina**

The TEM images showed below display the morphology and surface features of the MWCNTs incorporated in the matrices, after the heat treatment at 500 °C in air for 3 hours, to eliminate the surfactant and also the organic material that remained from the sol-gel process, and at the same time, we should provide that the interface between the MWCNTs and the matrix is good enough to preserve the good incorporation and dispersion of the MWCNTs within the matrix. Figure (a) shows the TEM image for MWCNT/alumina powder, where we can observe a very large MWCNT in length (about 2.0  $\mu\text{m}$ ) coming from inside the alumina matrix. It can also be seen that there is a coating on the surface of the MWCNT. Figure (b) shows, at a larger magnification, that effectively the MWCNTs are incorporated in the amorphous matrix and its surface is well coated. It was confirmed by EDS measurements, showed in the next Figure.





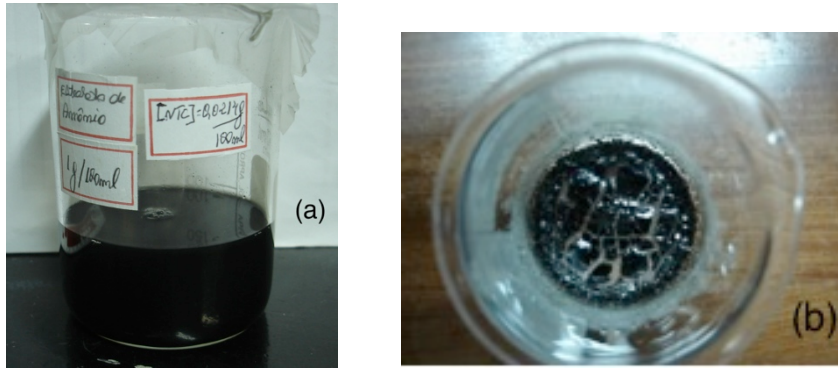
### MWCNTs/zirconia



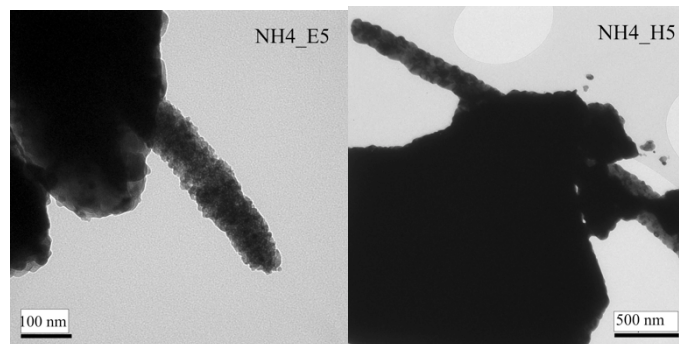


The Figure (a) above shows a MWCNT about 2.5  $\mu\text{m}$  in length, crossing the zirconia matrix, a magnification of this image is seen in Figure (b). It is impressive how homogeneous is the coating thickness if we compare to the coating obtained in the alumina matrix. It is possible also to estimate the diameter for the coated MWCNT as about 50 nm, almost in all length. It is noteworthy to mention that, when we make a heat treatment at 300  $^{\circ}\text{C}$  in MWCNTs/zirconia, we still have amorphous phase and the TEM images in this case are much like the ones obtained with amorphous alumina. However, in the case of zirconia, the heat treatment at 500  $^{\circ}\text{C}$  produced a tetragonal phase, with grain sizes of the order of  $20 \pm 3$  nm, and the CNTs are much better coated in this case.

For composites of MWCNTs/zirconia we used also two other kinds of surfactants, sodium and ammonium stearates, that are well known, cheap and easy to prepare, as dispersant agents for MWCNTs. In this case we used different quantities of MWCNTs added in the solution of water and the surfactant, and after that, this solution with the dispersed MWCNTs was added to the zirconia sol-gel, producing the composites with different concentrations of MWCNTs. Below there is in (a) the suspension of MWCNTs in the solution of ammonium stearate and water and in (b) the dried MWCNTs/zirconia gel with a concentration of 0.5 wt. % of MWCNTs.



The Figure below shows the TEM images for two samples, with 0.04 wt.% MWCNTs and 5.0 wt.% MWCNTs, respectively, heat-treated at 500 °C, where we have a tetragonal phase for zirconia. In this case the CNTs are completely coated by the matrix. From these images we can say that there is a good interface between the matrix and the CNTs, and that the crystallinity of the matrix plays an important role here, again. It is important to notice that these are selected images from several we have done presenting exactly the same behavior.



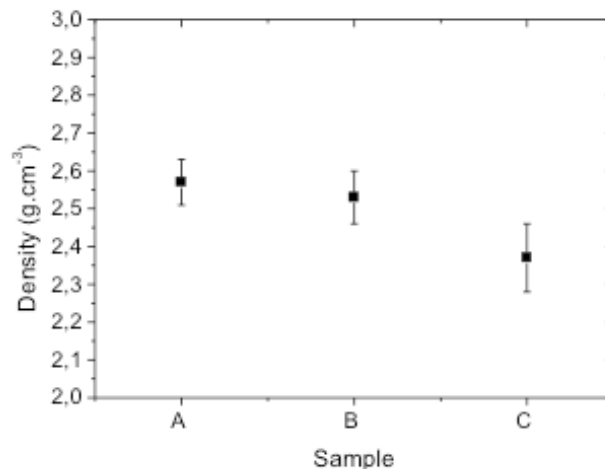
### High-pressure experiments

All the powders composites produced by sol-gel method were processed at high pressure (up to 7.7 GPa) at room temperature and at higher temperatures, from 200 °C to 1000 °C, using a toroidal high-pressure chamber assembled in a hydraulic 1000 Ton press. This work is still in development.

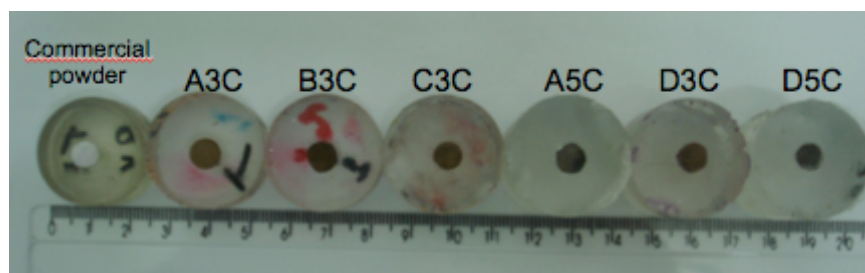
There are several samples to process at different conditions and measurements of Vickers microhardness, toughness and density are being done. As well as XRD, TEM and FTIR to investigate the nature of the interface between CNTs and the matrix.

Unfortunately we have only preliminary results, because we have some problems of maintenance of our hydraulic press that was out of order for almost 6 months.

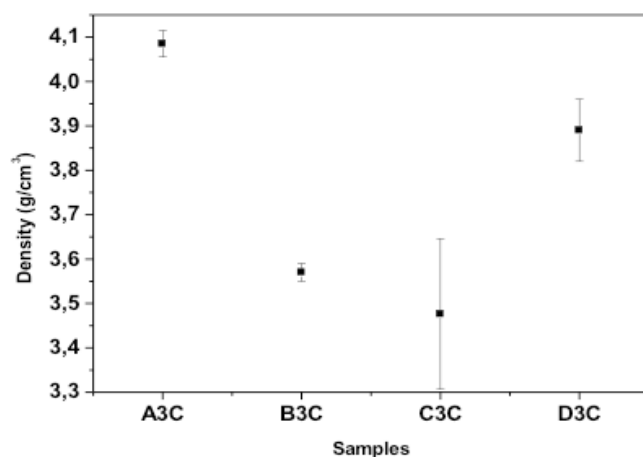
For MWCNTs/alumina compacted at 7.7 GPa at RT, which is still amorphous, it was obtained a microhardness of about 5.0 GPa, comparable to gamma alumina samples prepared at the same conditions. Below there is a plot with some density measurements, where A is pure alumina gel, B is alumina gel with surfactant and C is alumina gel with surfactant and MWCNTs. These are only preliminary results.



Below there are some of MWCNTs/zirconia composites heat-treated at 300 °C (A3C, B3C, C3C, D3C) and 500 °C (A5C, D5C) for 2 hours in air and compacted at 7.7 GPa at room temperature. They were inserted in a resin to make hardness measurements. They present different concentrations of CNTs, A is pure zirconia, B, C and D are with different CNTs concentrations with sodium stearate and E was made with ammonium stearate, with higher concentration of CNTs.



Below is a plot with density measurements for some of these samples.



I have to point out that these are only very preliminary results and the students are doing a hard work to process several samples at very different conditions, to look for the best conditions of pressure and temperature in order to obtain good samples with really improved properties, which is our final goal.

### **Archival papers published during Grant period and conferences**

Starting from 2009, all publications of our group explicit mention to the fact that our work is supported by the AFOSR.

1. Marina T. Laranjo, Master dissertation (in Portuguese) Entrapment of gold nanoparticles in sílica xerogels by high pressure technique, Federal University of Rio Grande do Sul, December 2009.
2. Pamela Mantey dos Santos, Master dissertation (in Portuguese) Investigation of the behavior of CNTs at high-pressure, UNIFRA, December 2010.

Works presented in the 48<sup>th</sup> EHPRG Conference in Uppsala, Sweden, July 25-29, 2010. Extended abstracts published in the Conference proceedings

3. Voltaire de O. Almeida, Wagner R. Fagundes, Patrícia R. Silva, Naira M. Balzaretti, Geraldo B. Machado, Tania M.H. Costa, Marcia R. Gallas, Incorporation of carbon nanotubes into a ZrO<sub>2</sub> matrix by sol-gel method and high pressure technique. (p.118)
4. Marina T. Laranjo, Edilson V. Benvenuti, Leticia Todeschine, Giovani R. rodrigues, Tarso B.L. Kist, Marcia R. Gallas, Tania M.H. Costa, Entrapment of gold nanoparticles in sílica xerogels by high pressure technique. (p.117)
5. Patricia R. Silva, Giovani R. Rodrigues, Wagner R. Fagundes, Tania M. H. Costa, Geraldo B. Machado, E. V. Benvenuti, Marcia R. Gallas, Carbon nanotube/alumina nanocomposite obtained by sol-gel method and high pressure technique. (p.115)

Works presented in the X Brazilian MRS Meeting (X SBPMat), September 25-29, 2011. Extended abstracts published in the Conference Book (on-line)

6. Voltaire de Oliveira Almeida, Naira Maria Balzaretti, Tania Maria Haas Costa, Geraldo Beyer Machado, Patrícia Rodrigues da Silva, Marcia Russman Gallas. Surfactants for CNTs dispersion in zirconia-based ceramic matrix obtained by sol-gel method.
7. Pâmela Andréa Mantey dos Santos, Ivana Zanella da Silva, Solange Binotto Fagan, Tania Maria Haas Costa, Marcia Russman Gallas. Study of the behavior of bulk carbon nanotubes at high pressure.
8. Patrícia Rodrigues da Silva, Giovani Ritta Rodrigues, Tania Maria Haas Costa, Geraldo Beyer Machado, Edilson V Benvenuti, Marcia Russman Gallas. Surfactant-based dispersant for multiwall carbon nanotubes to prepare alumina composites by sol- gel method.
9. Fabiano Severo Rodembusch, Sílvia Regina Grando, Fabiano da Silveira

- Santos, Marcia Russman Gallas, Tania Maria Haas Costa, Edilson Valmir Benvenutti Photophysics of aminobenzazole dyes in silica-based hybrid materials.
10. Alessandro Bof Oliveira, Patrícia Rodrigues da Silva, Pâmela Andréa Mantey Dos Santos, Tania Maria Haas Costa, Marcia Russman Gallas. An Approach for Quantifying Dispersion of Carbon Nanotubes in Ceramic Composites Using TEM images.

Additional works published:

11. M. T. Laranjo, T. B. L. Kist, E. V. Benvenutti, M. R. Gallas, T. M. H. Costa, Gold nanoparticles enclosed in silica xerogels by high-pressure processing, *J Nanopart Res* 13:4987–4995, 2011.
12. Hoffmann, Helena Sofia ; Stefani, Valter; Benvenutti, Edilson Valmir; Costa, Tania Maria Haas; Gallas, Marcia Russman . Fluorescent silica hybrid materials containing benzimidazole dyes obtained by sol gel method and high pressure processing. *Materials Chemistry and Physics* 126:97-101, 2011.
13. Grando, Silvia R.; Pessoa, Carolina M.; Gallas, Marcia R; Costa, Tania M. H.; Rodembusch, Fabiano S. ; Benvenutti, Edilson V. Modulation of the ESIPT Emission of Benzothiazole Type Dye Incorporated in Silica-Based Hybrid Materials. *Langmuir* 25:13219-13223, 2009.
14. Benvenutti, Edilson V. ; Moro, Celso C.; Costa, T.M. H.; Gallas, M. R. . Materiais híbridos a base de sílica obtidos pelo método sol-gel. *Química Nova* (in Portuguese), 32:1926-1933, 2009.
15. Mesquita, Alexandra ; Bernardi, Maria Inês B. ; Mastelaro, Valmor R. ; Lente, Manuel H. ; Eiras, José A. ; Gallas, Marcia R. ; Costa, Tania. M. H. . Nanograined Ferroelectric Ceramics Prepared by High-Pressure Densification Technique. *Journal of the American Ceramic Society*, 92: 1679-1683, 2009.

16. Rodrigues, Jaqueline C.; Costa, Tania Maria Haas ; Gallas, Márcia R.; Moro, Celso C. Influence of high-pressure processing on the structure and memory effect of synthetic layered double hydroxides. *Physics and Chemistry of Minerals*, 36,:439-446, 2009.
17. Kober, Umberto A.; Gallas, Márcia R.; Campo, Leandra F. ; Rodembusch, Fabiano S.; Stefani, Valter . Fluorescence emission modulation in singlefluoroforic submicro-sized silica particles. *Journal of Sol-Gel Science and Technology*, 52:305-308, 2009.

Works submitted for publication (2011) related to this project:

1. Patrícia R. Silva, Voltaire O. Almeida, Geraldo B. Machado, Edilson V. Benvenuti, Tania M. H. Costa, Márcia R. Gallas. A surfactant-based dispersant for multiwall carbon nanotubes to prepare ceramic composites by a sol-gel method. Submitted to *Langmuir*.
2. Voltaire O. Almeida, Naira M. Balzaretto, Tania M. H. Costa, Geraldo B. Machado, Márcia R. Gallas. Surfactants for CNTs dispersion in zirconia-based ceramic matrix by sol-gel method. Submitted to *J. Sol-Gel Science and Technology*.